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16. ABSTRACT

The rapid small-scale column test (RSSCT), a physical model of a fixed bed, was developed and evaluated experimentally to simulate full-scale adsorber performance. The RSSCT can simulate months of full-scale adsorber operation in several days; however, some isotherms and kinetic data are required for design. The dispersed flow, pore surface diffusion model (DFPSDM) was used to determine the proper adsorbent particle size, hydraulic loading, and empty-bed contact time of the RSSCT from the data from the full-scale adsorber. The experimental RSSCT breakthrough profiles for a six-solute mixture at influent concentrations between 3000 and 6000 u/L were identical to those of a pilot-scale column test. The RSSCT took only 4% of time that it took to conduct the pilot-scale column test.

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EPA/600/J-86/133
JOURNAL ARTICLE

Design of rapid small-scale adsorption tests for a constant diffusivity

John C. Crittenden, John K. Berrigan, David W. Hand

Recent attention to the impact of low-level contaminants on public health has encouraged a major research effort to develop effective means to identify, monitor, and remove toxic agents from drinking water, wastewater, and groundwater. Granular activated carbon (GAC) is an effective treatment technique for removal of some toxic organics from drinking water or wastewater. However, it can be a relatively expensive process, especially if designed improperly. The proper design of full-scale adsorbers typically includes time-consuming and expensive pilot-scale studies.

Accordingly, a rapid method for large-scale, fixed-bed adsorber design from small column studies, known as the rapid small-scale column test (RSSCT), was developed and evaluated. The three primary advantages of using small column studies for design are that an RSSCT may be conducted in a fraction of the time required to conduct pilot studies; unlike predictive mathematical models, extensive isotherm or kinetic studies are not required to obtain a full-scale performance prediction from an RSSCT; and a small volume of water is required to conduct the test which can be transported to a central laboratory for evaluation. Consequently, replacing a pilot study with an RSSCT significantly reduces the time and cost of a full-scale design. The benefits of RSSCT and the cost savings that are associated with proper design make it a very attractive alternative to a pilot study.

In the RSSCT method, mathematical models are used to scale-down the full-scale adsorber to an RSSCT and maintain perfect similarity between the performance of the adsorbers. If perfect similarity is maintained, the RSSCT, which uses a smaller adsorbent particle size than the full-scale adsorber, will have identical breakthrough profiles as the full-scale process. Accordingly, a number of RSSCTs could be used to evaluate the importance of design variables such as empty-bed contact time (EBCT) or bed operations such as beds in series or in parallel.

In this study, a dimensional analysis on the dispersed flow, pore surface diffusion model (DFPSDM) was used to determine scaling factors because the DFPSDM includes many of the known transport and kinetic phenomena that occur in fixed-bed adsorbers. Examination of the dimensionless groups in the DFPSDM showed that the adsorbent particle sizes of the RSSCT and full-scale bed determined the scaling relationships between hydraulic loadings and EBCTs of the RSSCT and full-scale columns.

The scaling procedure was verified by both model calculations and experimental data. Example calculations for an RSSCT and a full-scale adsorber with the DFPSDM and the homogeneous solid diffusion model (HSDM) demonstrated that identical breakthrough profiles for single component and multicomponent systems would be obtained. These calculations proved that an RSSCT could be designed to simulate a full-scale adsorber in 1.05% of the time of a pilot-scale study. The RSSCT was verified experimentally by comparing a pilot-scale adsorber to an RSSCT. A six-solute mixture with individual concentrations from 3000 to 6000 μg/L was used. The RSSCT data were identical to the pilot data and this demonstrated experimentally that the RSSCT can be run in 4% of the time required for a pilot study. However, surface diffusivity was identical for both GACs used in the RSSCT and in the full-scale application for this study.

In another study, four RSSCTs were conducted and it seemed that the surface diffusivities for GAC used in RSSCTs were not identical to the surface diffusivity for the GAC that was to be used in the full-scale plant. Berrigan[1,2] and Crittenden *et al.*[3] discuss the design considerations of an RSSCT for that situation. A procedure that is modified from the one in this study was used by Berrigan[1,2] and Crittenden *et al.*[3] and the resulting breakthrough profiles from the RSSCT were identical to the breakthrough profiles of corresponding pilot-scale adsorbers treating the same groundwater.

MATERIALS AND METHODS

To experimentally evaluate the accuracy of this procedure in predicting the breakthrough profiles of a large adsorber, an RSSCT was designed to simulate the performance of a pilot-scale adsorber. The particle size for the RSSCT was selected to be as small as possible thus shortening the duration of the experiment and yet be large enough to maintain a practicable sampling schedule and avoid excessive headloss.

Full-scale adsorber performance can be predicted in less time and at less cost by plotting effluent concentration in terms of bed volumes fed.

Apparatus and materials. All laboratory column experiments were conducted at 10°C, a typical groundwater temperature for the northern U. S. These experiments were performed in a temperature-controlled room where maximum temperatures of 12°C were measured. All experimental equipment was constructed of glass, nonreactive fluorocarbon polymers, or stainless steel to minimize adsorption of organics.

Glass columns with 5.0-cm and 1.1-cm diameters were used for pilot-scale and RSSCT studies, respectively. The effects of

channeling and wall effects were avoided by exceeding the ratio of the particle diameter to column diameter at approximately 50.[4]

Feed solutions for the laboratory studies were prepared by mixing a concentrated aqueous solution of the volatile organic chemicals with laboratory reagent water in a headspace-free, mixing vessel before being fed into the column. The concentrated solution and dilution water were applied to the mixing vessel with positive displacement metering pumps. The pH of the influent and effluent was monitored occasionally throughout the laboratory experiments and was 6.5. Experimental details are given by Berrigan *et al.*[1,2]

All chemicals were reagent grade or better. A bituminous-based GAC that contained a significant amount of macropores was used in this study. Water for influent and other solution preparation was distilled, deionized, and filtered through activated carbon.

Chemical analysis. The volatile organic compounds (VOCs) were analyzed using a gas chromatograph equipped with an electron capture detector. Following the procedure described by Mieure,[5] a liquid-liquid extraction (LLE) procedure was developed. The samples for LLE method were extracted using 5 to 30 mL of solution with 5 to 10 mL 2,2,4-trimethylpentane. The internal standard for the LLE method was 1,1,1-trichloroethane.

Carbon preparation. Representative samples of GAC were obtained by mixing and splitting the GAC. The GAC from these samples, U. S. No. 12 × 40 mesh, was used in the pilot-scale work. A smaller activated carbon, 60 × 80 mesh, was used in RSSCT studies. The smaller carbon for the RSSCT experiments was obtained by crushing samples of the original carbon, U. S. No. 12 × 40, to a smaller size. The crushed carbon was sieved, retaining the U. S. No. 60 × 80 mesh size and recrushed. The crushing and sieving was continued until all the carbon had passed through the 60 mesh sieve tray. The GAC retained on an 80-mesh sieve was then washed with high purity water and dried overnight at 105°C.

APPROACH

Several researchers[6-8] have used mathematical models and governing equations to define scaling relationships of the design and operational parameters between the small- and full-scale processes. Beckner[9] discusses many other contributions to the subject. In summary, three conditions are applied to the governing equations of a system so that the design and operation of a small-scale process give similar operating data to that of the full-scale process. First, boundary conditions for the large- and small-scale processes must occur at the same dimensionless coordinate values in the dimensionless differential equations. Second, dimensionless parameters in the dimensionless differential equations for the full-scale process must equal those for the small-scale process. Finally, no change in mechanism can occur with the change in process size.

The RSSCT scale-up was based on the DFPSDM because it contains many of the phenomena that occur in fixed-bed adsorbers[10] namely, axial dispersion, axial advective flow, surface diffusion, pore diffusion and liquid-phase mass transfer resistance. Furthermore, if exact similarity can be guaranteed for the DFPSDM, then similarity will exist for simpler models, for example, the plug-flow, pore surface diffusion model (PFPSDM) which ignores axial dispersion, and the dispersed-flow homogeneous solid diffusion model (DFHSDM) which lumps pore and surface diffusion together, or the plug-flow homogeneous solid diffusion model (PFHSDM).

In the past, the PFHSDM has been shown to predict adsorption, desorption, and multicomponent competition in fixed beds.[11-16] Crittenden *et al.*[14] and Thacker *et al.*[14,15] discussed recent work in which the PFHSDM has been used to predict fixed-bed performance.

Using the DFPSDM, the three conditions of similarity can easily be applied to the model equations in dimensionless form to design a small-scale adsorber that yields operating data similar to that of the full-scale process. In the section on the DFPSDM, model equations are in dimensionless form such that the boundary conditions for the large- and small-scale processes occur at the same dimensionless coordinate values in the DFPSDM. In the section on the development of the scaling equations, the dimensionless parameters from the model equations for the full-scale process are equated to those for the small-scale process. Accordingly, if no change in mechanism occurs with a change in process size then all three conditions will be met for similarity.

Previous work. A small column technique has been used successfully by Beaudet *et al.*,[18] Billelo *et al.*,[19] and Rosene *et al.*[20] to determine carbon usage rates. These methods use a fixed-bed column of fine mesh carbon and high pressure liquid chromatography (HPLC). This technique also provides qualitative information on the order of breakthrough for multicomponent mixtures. However, these investigators have not provided a method that would accurately forecast breakthrough profiles of the full-scale process using their small fixed-bed results.

Frick[21] proposed a method of interpreting small-scale adsorber information with scaling equations based on Stanton number and the solid diffusion modulus, E_d. The scaling equations that result account for mass-transport mechanisms of solid diffusion, liquid film transfer, and advection. A small-scale experimental test could be designed from these equations to simulate full-scale adsorber performance and provide a theoretical starting point for the work in this study.

Dispersed flow pore surface diffusion model. The DFPSDM incorporates the following mechanisms: advective flow, axial dispersion and diffusion (this may be important when mass transfer rates are high or when low flow rates occur in the RSSCT), liquid-phase mass transfer resistance, local adsorption equilibrium at the exterior surface of the adsorbent, surface diffusion, pore diffusion, and competitive equilibrium of solutes on the carbon surface (competitive effects are assumed to be fully accounted for by multi-solute equilibrium expressions and there are no diffusion multicomponent interactions).

For DFPSDM calculations, equilibrium isotherm equations are needed to describe multicomponent interactions. To estimate the competitive effects of solutes on the adsorbent surface in DFPSDM calculations, ideal adsorbed solution theory (IAST)[11,15,22] was used to describe multi-solute competition. Crittenden *et al.*[23] confirmed that IAST could be used to predict competitive interactions between VOCs. Competitive interactions in fixed-beds do not need to be described by IAST for the proposed scaling procedure to work. The only requirement is that the capacity of the GAC cannot depend on the sizes that are used in the RSSCT and the full-scale process. The IAST equations are presented here only for completeness.

If the Freundlich isotherm equation is used to describe single solute behavior, IAST yields the following equation for each adsorbate:

$$\bar{C}_{p,i}(\bar{r}, \bar{z}, T) = \left[\frac{\bar{Y}_i(\bar{r}, \bar{z}, T) Y_{e,j} - \frac{\epsilon_p}{\rho_a} \bar{C}_{p,i}(\bar{r}, \bar{z}, T) C_{o,j}}{C_{o,j} \sum_{j=1}^{m} \left[\bar{Y}_j(\bar{r}, \bar{z}, T) Y_{e,j} - \frac{\epsilon_p}{\rho_a} \bar{C}_{p,j}(\bar{r}, \bar{z}, T) C_{o,j} \right]} \right] \times \left[\frac{\sum_{k=1}^{m} \left[n_k \left[\bar{Y}_k(\bar{r}, \bar{z}, T) Y_{e,k} - \frac{\epsilon_p}{\rho_a} \bar{C}_{p,j}(\bar{r}, \bar{z}, T) C_{o,i} \right] \right]}{n_i K_i} \right]^{n_i} \quad (1)$$

Variable definitions for all equations are found in the Appendix. Equation 1 was used to couple the liquid and solid phase concentrations at both the internal and external adsorbent surfaces.

The DFPSDM, Equations 2 through 9, describe the fate of an adsorbate, i, within a fixed-bed adsorber. Friedman[10] gives a complete derivation and solution of these equations. The liquid-phase mass balance for each adsorbate in dimensionless form is

$$-\frac{\partial \bar{C}_i(\bar{z}, T)}{\partial \bar{z}} + \frac{1}{Pe_i} \frac{\partial^2 \bar{C}_i(\bar{z}, T)}{\partial \bar{z}^2} = \frac{1}{(Dg_i + 1)} \frac{\partial \bar{C}_i(\bar{z}, T)}{\partial T} + 3St_i[\bar{C}_i(\bar{z}, T) - \bar{C}_{p,i}(\bar{r} = 1, \bar{z}, T)] \quad (2)$$

The terms in Equation 2 account for advective flow, axial dispersion and diffusion, accumulation in the liquid phase, and transport from the liquid to the solid phase by liquid-phase mass transfer. The initial condition for Equation 2 is

$$\bar{C}_i(0 \le \bar{z} \le 1, T = 0) = 0 \quad (3)$$

The boundary conditions for the liquid-phase mass balance are those proposed by Danckwerts[24]

$$1 - \bar{C}_i(\bar{z} = 1, T) = \frac{1}{(Dg_i + 1)} \frac{\partial}{\partial T} \left[\int_0^1 \left[\bar{C}_i(\bar{z}, T) + 3Dg_i \int_0^1 \bar{Y}_i(\bar{r}, \bar{z}, T) \bar{r}^2 d\bar{r} \right] \partial \bar{z} \right] \quad (4)$$

$$\frac{\partial^2 \bar{C}_i(\bar{z} = 1, T)}{\partial \bar{z} \partial T} = 0 \quad \text{and} \quad \frac{\partial \bar{C}_i(\bar{z}, T = 0)}{\partial \bar{z}} = 0 \quad (5)$$

Equations 4 and 5 are derived from equating the mass flux entering and leaving the bed, assuming that transport of the adsorbate into or out of the fixed-bed by axial dispersion and diffusion is negligible when compared to advection. (This is usually referred to as a closed vessel.)

The intraparticle mass balance is expressed by

$$\frac{1}{\bar{r}^2} \frac{\partial}{\partial \bar{r}} \left[\bar{r}^2 \left[(Ed_{s,i} + D_i Ed_{p,i}) \frac{\partial \bar{Y}_i(\bar{r}, \bar{z}, T)}{\partial \bar{r}} + (Ed_{p,i} - D_i Ed_{p,i}) \frac{\partial \bar{C}_{p,i}(\bar{r}, \bar{z}, T)}{\partial \bar{r}} \right] \right] = \frac{Dg_i}{Dg_i + 1} \frac{\partial \bar{Y}_i(\bar{r}, \bar{z}, T)}{\partial T} \quad (6)$$

The terms in Equation 6 account for surface and pore diffusion, and accumulation in the intraparticle phase, respectively. The initial condition for Equation 6 is

$$\bar{Y}_i(0 \le \bar{r} \le 1, 0 \le \bar{z} \le 1, T = 0) = 0 \quad (7)$$

The boundary conditions for Equation 6 are

$$\frac{\partial}{\partial \bar{r}} \bar{Y}_i(\bar{r} = 0, 0 \le \bar{z} \le 1, T \ge 0) = 0 \quad (8)$$

$$\frac{Dg_i}{Dg_i + 1} \frac{\partial}{\partial t} \int_0^1 \bar{Y}_i(\bar{r}, \bar{z}, T) \bar{r}^2 d\bar{r} = St_i[\bar{C}_i(\bar{z}, T) - \bar{C}_{p,i}(\bar{r} = 1, \bar{z}, T)] \quad (9)$$

Equation 8 results from symmetry. In Equation 9, the liquid-phase mass flux is equated to the intraparticle-phase mass flux.

Development of scaling equations. Six independent dimensionless quantities, $Dg_{s,i}$, $Dg_{p,i}$, $Ed_{s,i}$, $Ed_{p,i}$, Pe_i, and St_i are contained in Equations 1 through 9. For perfect simulation of a full-scale adsorber, each of the six independent dimensionless groups must remain constant as a full-scale adsorber is scaled to the size of an RSSCT. By setting the dimensionless groups of a small-scale RSSCT adsorber (SC) equal to those of a large-scale column (LC), relationships between key design variables were found.[2]

To obtain the scaling relationships, assumptions must be made about changes in phenomena that may affect process performance. Four phenomena that could change with fixed-bed adsorber size are the effects of backwashing, physical characteristics of the GAC, adsorption equilibrium capacity, and adsorption kinetics. These phenomena could produce a poor representation of a full-scale adsorber performance by the RSSCT. The impact of backwashing was not considered in scaling equation development and is not discussed in this work. However, it may be possible to simulate backwashing in the RSSCT, if the adsorbent particles were distributed in a similar fashion during and after backwashing in the RSSCT and full-scale adsorbers.

Table 1—Comparison of design and operational parameters of a full-scale column and a rapid small-scale column test (RSSCT) which is designed to simulate full-scale performance.

	Full-scale adsorber	RSSCT
GAC packing characteristics		
ρ_a	803.4 kg/m³	803.4 kg/m³
ϵ	0.40	0.40
R	5.13×10^{-4} m	5.25×10^{-5} m
Column and flow specifications		
Column diameter	2.44 m	0.00525 m
Column length	0.417 m	0.0426 m
EBCT	300 s	3.14 s
Cross-sectional area	4.67 m²	2.16×10^{-5} m²
v_a	5.00 m/h	48.9 m/h
Bed volume	1.946 m³	9.23×10^{-7} m³
Flow rate	6.483 L/S	2.93×10^{-4} L/S
Required volume to simulate 72 800 bed volumes of feed	1.42×10^{5} m³	0.0672 m³
Run time to simulate 72 800 bed volumes of feed	252 days	2.65 days
Head loss	591 N/m² 0.10 psi	56 400 N/m² 8.18 psi

Table 2—Chemical and dimensionless parameters for a full-scale column and a RSSCT for *cis*-dichloroethylene (DCE), trichloroethylene (TCE), tetrachloroethylene (PEC), toluene, and xylene. The column parameters may be found in Table 1 under the headings of full-scale adsorber and RSSCT which is designed to simulate the full-scale adsorber.

	DCE	TCE	PCE	Toluene	Xylene
C_o, μmol/L	0.413	1.52	0.9045	1.042	0.474
K, μmol/g(L/μmol)$^{1/n}$	39.0[a]	196.6[a]	650.0[b]	300.0[b]	1500.0[b]
$1/n$	0.7045	0.4163	0.4579	0.4400	0.3500
D_s, m^2/s	7.17×10^{-14}	3.75×10^{-14}	7.41×10^{-15}	2.36×10^{-14}	6.28×10^{-15}
D_p, m^2/s	9.72×10^{-6}	9.97×10^{-6}	1.02×10^{-5}	1.01×10^{-7}	1.03×10^{-5}
k_f full-scale, m/s	2.23×10^{-3}	2.07×10^{-3}	1.95×10^{-3}	2.00×10^{-3}	1.88×10^{-3}
k_f RSSCT, m/s	2.14×10^{-4}	1.98×10^{-4}	1.87×10^{-4}	1.85×10^{-4}	1.74×10^{-4}
Pe	149.0	145.0	142.0	143.0	140.0
St	7.83	7.27	6.84	7.03	6.63
Bi	3.91	2.29	2.44	1.84	0.786
E_d	2.00	3.18	2.81	3.81	8.43

[a] Measured by Luft[16] and Crittendon *et al.*[23]

[b] Determined from Dobbs and Cohen[37] by accounting for temperature change and inadequate equilibration time.[1,16]

With respect to equilibrium capacity, exact similarity between the RSSCT and the full-scale adsorber can be achieved if the isotherm capacity of small GAC which is used in the RSSCT is identical to the full-scale adsorber GAC. Adsorption capacity has been shown not to depend on particle size many times in the literature, if adequate equilibration time is given and a representative GAC sample is used.[14,15,25,26] Berrigan *et al.*[2] demonstrated, that if the GAC preparation procedure that is summarized in the experimental methods section is used to obtain GAC for the RSSCT, then the isotherm capacity for the RSSCT GAC is identical to that noted in the unground GAC.

The physical characteristics of the GAC (apparent and bulk density and bed void fraction) were demonstrated to have little impact on the performance which would be predicted using the RSSCT for the small differences that were observed.[1,2]

The final phenomena that could change with process size is adsorption kinetics. The development of proper scaling equations required assumptions of the relationship between adsorbent particle radius and the pore and surface diffusion coefficients, D_s and D_p, respectively. Dobrzelewski *et al.*[27] conducted rate studies for trichloroethene (TCE) at concentrations of 10.0 μmol/L, and found that D_p and D_s did not significantly depend on particle radius. Accordingly, the scaling equations and experimental verification work assume that surface diffusion coefficients do not depend on particle size. For the case where there is no change in D_s and D_p with scale-down, perfect similarity may be achieved.

However, in another RSSCT study, Berrigan[1] and Crittenden *et al.*[3] found that D_s may depend on particle size and a method was proposed to scale down the RSSCT assuming that the mass transfer rate was controlled by surface diffusion. This procedure was verified experimentally and discussed in detail by Berrigan[1,2] and Crittenden *et al.*[3] Consequently, the method that is proposed in this report is only valid for the situation in which the GAC surface and pore diffusivities that are used in RSSCT are identical to those used in the full-scale plant. This should be verified using several solutes and concentrations of interest, and methods that are described by Hand *et al.*[28] and Dobrzelewski *et al.*[27]

By equating the surface diffusivity modulus, $Ed_{s,i}$, and the pore diffusivity modulus, $Ed_{p,i}$ of a small column to that of a full-scale adsorber, the proper relationship between the small column and large column empty-bed contact times (EBCTs) may be found.

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{R_{SC}}{R_{LC}}\right]^2 = \frac{t_{SC}}{t_{LC}} \qquad (10)$$

Berrigan[1] and Berrigan *et al.*[2] provided the details of scaling equation development. The relationship defined in Equation 10 is valid for various combinations of mass transfer resistance that control the intraparticle resistance: pore diffusion, surface diffusion, or both pore and surface diffusion control.

To obtain Equation 10, the solute distribution parameters, Dg_i, were assumed to be the same for carbons in the small- and full-scale processes. This is valid if the equilibrium capacity, the bed void fractions, the particle densities, and the influent concentrations are all identical. The ratio t_{SC}:t_{LC} is the time required

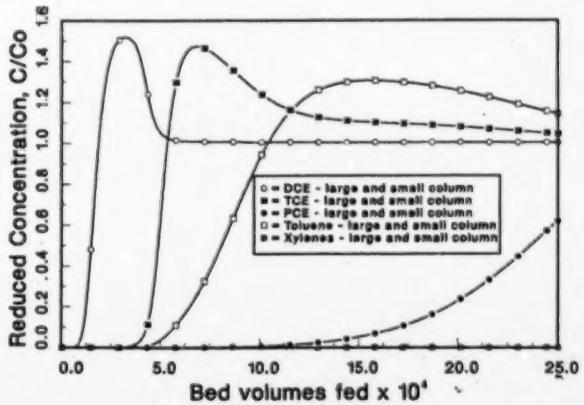

Figure 1—DFHSDM effluent profile predictions for the rapid small-scale column test and full-scale adsorber assuming a constant surface diffusivity.

to conduct an RSSCT divided by the time it takes to conduct a pilot study. According to Equation 10, the magnitude of the time savings for the RSSCT is determined by the magnitude of the size reduction of the original GAC in the full-scale system for the RSSCT.

Similarly, to have identical Stanton numbers, St_i, the liquid-phase mass transfer coefficients may be related by the following equation:

$$\frac{k_{f,SC}}{k_{f,LC}} = \frac{R_{LC}}{R_{SC}} \tag{11}$$

To satisfy the constraints of Equation 11, small- and large-column Sherwood numbers must be equal for all of the adsorbates. Most liquid-phase mass transfer correlations[29] have the following general form:

$$Sh_i = F(Re_i, Sc_i) \tag{12}$$

The correlations of Wilson and Geankopolis[30] and Williamson and Geankopolis[31] have been shown to accurately determine film transfer coefficients in fixed-bed adsorbers.[11,12,14,15,17] Both correlations have the form of Equation 12. Consequently, the hydraulic loading of the small- and large-scale columns are related to the particle size by this expression

$$\frac{V_{SC}}{V_{LC}} = \frac{R_{LC}}{R_{SC}} \tag{13}$$

Table 3—Pilot-scale and small-scale design parameters.

	Large column	RSSCT
GAC packing characteristics		
ρ_b	478 Kg/m^3	482 Kg/m^3
ϵ	0.40	0.40
R	5.13 × 10^{-4} cm	1.05 × 10^{-4} cm
Flow specifications		
Column diameter	0.050 m	0.011 m
Column length	0.0833 m	0.017 m
EBCT	60 s	2.51 s
CSA	1.96 × 10^{-2} m^2	9.50 × 10^{-3} m^2
V_s	5.00 m/h	24.4 m/h
Bed volume	0.164 L	1.62 × 10^{-3} L
Flow rate	0.164 L/min	0.0387 L/min
Required volume to simulate 16 000 bed volumes of feed	2618 L	25.9 L
Run time to simulate 16 000 bed volumes of feed	11.1 days	0.466 days
Head loss	118 N/m^2	3220 N/m^2
	0.02 psi	0.47 psi
Average influent concentrations µg/L		
Chloroform	2609	2670
TCE	3397	3763
Chlorodibromomethane	5367	5293
1,2 Dibromoethane	5730	5845
Bromoform	4366	4731
PCE	2281	3018
Influent Temperature	11 ± 1°C	11 ± 1°C

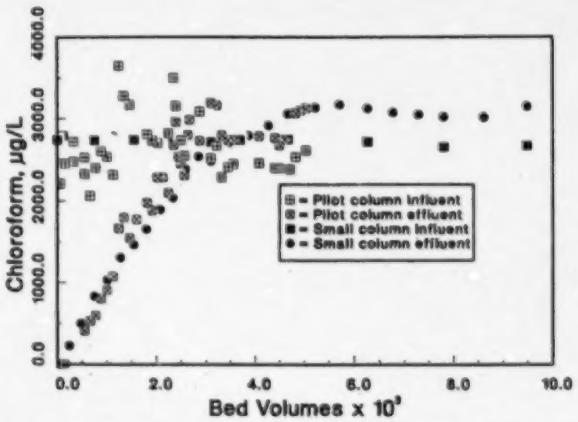

Figure 2—Comparison of the chloroform effluent profiles for the rapid small-scale column test and pilot-scale columns.

Equation 13 ensures that the Reynolds number of the small-scale process is the same as the large-scale process. Because the Reynolds and Schmidt numbers are identical for the large- and small-scale columns, Fried,[32] Ebach and White,[33] and Miyuachi and Kikuchi[34] have shown that Peclet numbers, based on particle size, Pe_d, will be identical. Furthermore, the column length to particle size ratios, L:R, for the small- and large-scale columns are equal. This implies that the small- and large-scale column have equal Peclet numbers that are based on column length (Pe_L). Equation 13 guarantees exact similarity whether plug flow or dispersed flow conditions exist.

RESULTS AND DISCUSSION

Theoretical verification. Friedman[10] demonstrated that pore diffusion was unimportant for the column conditions similar to those reported in Tables 1 and 2. Consequently, to illustrate the applicability of the scaling procedure, the DFHSDM was used to predict the multicomponent effluent concentration history profiles of the large-scale adsorber and the RSSCT which was designed to simulate full-scale performance. Computer algorithms are described by Friedman.[10] The design and operational parameters are given in Table 1. The influent contained *cis*-dichloroethylene (DCE), TCE, tetrachloroethene (PCE), toluene, and xylene at concentrations near those measured in a related field study.[1,2] The chemical, mass transfer and dimensionless parameters for these adsorbates are shown in Table 2. The surface diffusivities for components other than TCE were calculated using the correlation developed by Dobrzelewski *et al.*[27] The RSSCT and large-scale dimensionless parameters are identical; therefore, only one set of parameters is given for each adsorbate. As shown in Figure 1, the breakthrough profiles for the RSSCT and large-scale adsorber are identical for each component in Table 1. In theory, then, the RSSCT can be conducted in 1.05% of the time required for a pilot-scale adsorber, regardless of the adsorbate mixture, if the GAC particle radius is reduced from 0.0513 cm to 0.00525 cm and the surface diffusivity is identical for the small and large GAC particle sizes.

Experimental verification. The scaling procedure was verified by comparing performances of a pilot-scale adsorber to an

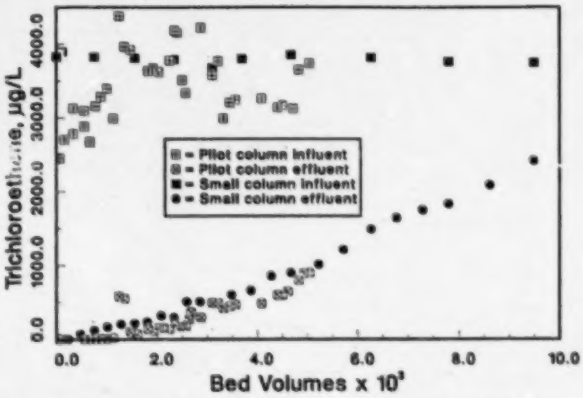

Figure 3—Comparison of the trichloroethene effluent profiles for the rapid small-scale column test and pilot-scale columns.

RSSCT with U. S. No. 60 × 80 mesh size GAC. The design and operational parameters are listed in Table 3. This six component mixture given here in order of increasing adsorptability was used to test the predictive ability of the RSSCT—chloroform, chlorodibromomethane, 1,2-dibromoethane, bromoform, TCE, and PCE. The influent and effluent concentrations for three of the six components for the pilot-scale adsorber and the RSSCT were plotted in Figures 2 through 4. As shown in Figures 2 through 4, the RSSCT influent concentration was more consistent than that of the pilot plant because the pilot-plant influent was made by mixing a concentrated feed with dilution water and the influent for the RSSCT was made in one batch. The pilot-scale adsorber study which required 818 L of water for 3.47 days of operation was only conducted for 5000 bed volumes of treatment because mechanical failure forced the end of operation. However, in 24 hours, the small-scale adsorber had treated 33 000 bed volumes using only 60 L of water. As shown in Figures 2 through 4, agreement between the pilot-scale adsorber and RSSCT effluent concentration profiles was good. Agreement for the other three components which are not shown was just as good.[23] Slight discrepancies between breakthrough profiles for the pilot-scale adsorber and the RSSCT seem to correspond with differences in influent concentrations that are plotted in Figures 2 through 4 and summarized in Table 3. Consequently, an RSSCT that uses 60 × 80 mesh GAC can be conducted in 4.2% of the time that the pilot-scale column can be conducted.

CONCLUSIONS

Full-scale adsorber performance may be predicted in less time and at less expense with RSSCT than with a pilot study by plotting the effluent concentration history in terms of the bed volumes fed. The RSSCTs use a smaller size GAC that is prepared from GAC to be used in the full-scale process.

Several RSSCTs may be used to rapidly evaluate several EBCTs of important process configurations such as beds in series or in parallel. To select the least expensive adsorber operation, both the fixed-bed adsorber configuration and EBCT have to be selected. In the design of pulsed-beds or beds in series, the EBCT of the mass transfer zone (MTZ) needs to be determined. Following the procedure discussed by Hand *et al.*[35] and Crittenden and Hand,[36] the breakthrough profiles of the RSSCT could be used to estimate the EBCT of the MTZ of the large adsorber for a single component, if a constant pattern exists. Lee *et al.*[26] and Crittenden and Hand[36] discussed the proper selection of the adsorber design variables. Accordingly, RSSCT should be configured to assess the performance of fixed-bed operations.

Like pilot studies, RSSCT will match full-scale performance only if GAC used in the full-scale adsorber has the same equilibrium capacity, and bulk density as that used in RSSCT. Also like pilot studies, RSSCT can simulate the full-scale system only if operating temperatures and influent concentrations are the same.

Scaling equations were derived from dimensionless groups found in the DFPSDM. The choice of a reduced size carbon determines the proper hydraulic loading rate and EBCT for the RSSCT. Perfect similarity between RSSCT and the full-scale adsorber may be achieved if surface diffusivity for a representative influent solute on the RSSCT GAC is the same as that on the full-scale GAC. This must be demonstrated for similar compounds and concentrations because in another study, Crittenden *et al.*[2,3] discovered that there seemed to be a difference in GAC surface diffusivities that were used in the full-scale adsorber and RSSCT. Crittenden *et al.*[2,3] also developed scaling equations for that case.

A batch-rate study should be conducted according to Hand *et al.*[28] The easiest way to decide whether the surface diffusivities for the full-scale and RSSCT GACs are identical is to plot concentration versus t/R^2 because this does not require an isotherm test. Profiles for both GACs should be identical when plotted in this manner if their intraparticle diffusivities are identical.

If surface diffusivities are identical, then an RSSCT can be designed using only Equations 10 and 13. Model calculations were made with the DFHSDM, and identical breakthrough profiles were given for an RSSCT and a full-scale adsorber that were treating a five-component mixture. Therefore, in theory, RSSCT can be conducted in 1.05% of the time required for a pilot-scale adsorber, regardless of the adsorbate mixture, if the GAC particle radius is reduced from 0.0513 cm to 0.00525 cm and the surface diffusivity is identical for the small and large GAC particle sizes.

Measurement of the TCE surface diffusivities in GACs that were to be used in the pilot-scale and RSSCT studies indicated that it was possible to design an RSSCT to perfectly simulate larger adsorber performance. Accordingly, a laboratory verifi-

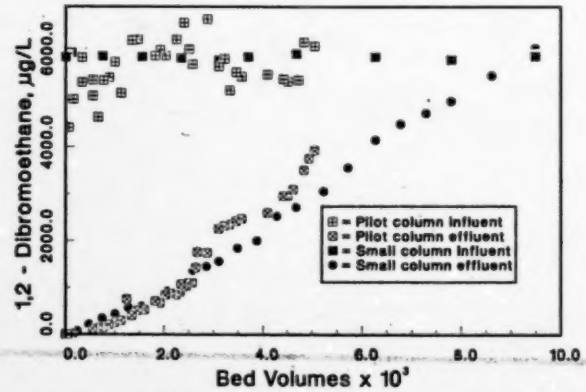

Figure 4—Comparison of the 1,2-dibromoethane effluent profiles for the rapid small-scale column test and pilot-scale columns.

cation of the RSSCT was conducted and agreement between the laboratory pilot-scale adsorbers and the RSSCT breakthrough profiles was good. The RSSCT that was conducted with U. S. No. 60 × 80 mesh (0.0105 cm) GAC was conducted in 4.2% of the time that the pilot-scale column was conducted. Before this method is considered generally applicable, more field testing is required[2,3] because it seems that it may be possible to prepare a smaller mesh GAC for use in an RSSCT that will give identical results as a pilot test.

APPENDIX

$Bi_{s,i}$ = Biot number based on surface diffusivity (dimensionless); $Rk_{f,i}(1 - \epsilon)/(D_{s,i}Dg_{s,i}\epsilon)$.

BVF = bed volumes of feed (dimensionless).

BVF_{max} = maximum number of bed volumes that can be treated (dimensionless).

$\bar{C}_i(\bar{z}, T)$ = reduced adsorbate concentration in bulk phase as a function of dimensionless axial position and dimensionless time (dimensionless); $C_i(z, t)/C_{o,i}$.

$C_{o,i}$ = initial influent bulk phase concentration (μg/L).

$\bar{C}_{p,i}(\bar{r}, \bar{z}, T)$ = reduced adsorbate concentration in adsorbent pores as a function of dimensionless radial and axial position and dimensionless time (dimensionless); $C_{p,i}(r, z, t)/C_{o,i}$.

CSA = cross-sectional area of adsorber (m^2).

De_i = axial dispersivity based on adsorber length and interstitial velocity (m^2/s).

Dg_i = combined solute distribution parameter (dimensionless); $(Dg_{s,i} + Dg_{p,i})$.

$Dg_{p,i}$ = pore solute distribution parameter (dimensionless); $\epsilon_p(1 - \epsilon)/\epsilon$.

$Dg_{s,i}$ = surface solute distribution parameter (dimensionless); $\rho_a q_{e,i}(1 - \epsilon)/\epsilon C_{o,i}$.

Dg_t = total solute distribution parameter (dimensionless); $(Dg_{p,i} + Dg_{s,i})$ over all components.

D_i = ratio of surface to pore diffusion transport (dimensionless); $(Ed_{s,i}Dg_{p,i})/(Ed_{p,i}Dg_{s,i})$.

D_L = free liquid diffusivity (m^2/s).

$D_{p,i}$ = pore diffusivity based on pore void fraction (m^2/s).

$D_{s,i}$ = surface diffusivity (m^2/s).

Dia = column diameter (m).

$EBCT$ = τ/ϵ, V_B/Q or L/V_s, fluid residence time in the bed which is devoid of the adsorbent or empty bed contact time (min).

$Ed_{p,i}$ = pore diffusion modulus (dimensionless); $D_{p,i} \times Dg_{p,i}\tau/R^2$.

$Ed_{s,i}$ = surface diffusion modulus (dimensionless); $D_{s,i} \times Dg_{s,i}\tau/R^2$.

i = subscript denoting a solute i.

K_i = Freundlich isotherm capacity constant [μg/g(L^3/μg)$^{1/n}$].

$k_{f,i}$ = film transfer coefficient (m/s).

$1/n_i$ = Freundlich isotherm intensity constant (dimensionless).

L = length of fixed-bed (m).

Pe_i = Peclet number based on interstitial velocity and adsorber length (dimensionless); Lv/De_i.

$Pe_{i,D}$ = $2vR/D_e$, Peclet number based on particle diameter (dimensionless).

$Pe_{i,miz}$ = vL_{miz}/D_e, Peclet number based on length of the mass transfer zone (dimensionless).

$q_{e,i}$ = adsorbent phase concentration in equilibrium with initial bulk phase concentration (μg/g); $K_i C_{o,i}^{1/n_i}$.

$\bar{q}_i(\bar{r}, \bar{z}, T)$ = reduced adsorbent phase concentration as a function of dimensionless radial and axial position and dimensionless time (dimensionless); $q_i(r, z, t)/q_{e,i}$.

Q = fluid flow rate (L/s).

r = radial coordinate (m).

$\bar{r}$ = reduced radial coordinate (dimensionless); r/R.

R = adsorbent radius (m).

Re = Reynolds number (dimensionless).

Sc = Schmidt number (dimensionless).

Sh_i = $k_{f,i}2R/D_L$, Sherwood number (dimensionless).

St_i = modified Stanton number (dimensionless); $k_{f,i}\tau(1-\epsilon)/R\epsilon$.

$St_{i,min}$ = minimum Stanton number required to establish constant pattern (dimensionless).

t = elapsed time (m).

$\bar{T}$ = reduced time (mass throughput) (dimensionless); $t/\tau(Dg_t + 1)$ used in fixed-bed models.

v = interstitial velocity (m/s); v_s/ϵ.

v_s = superficial velocity (m/s).

V_b = molal volume at the normal boiling point (cm^3/g · mole).

V_B = volume of the bed (m^3).

V_p = pore volume per mass of adsorbent (cm^3/g).

$Y_{e,i}$ = total adsorbent phase concentration in equilibrium with initial bulk phase concentration; $q_e + \epsilon_p C_{io}/\rho_a$.

$Y_i(r, t)$ = total adsorbent phase concentration as a function of radial position and time; $q_i(r, t) + [\epsilon_p C_{p,i}(r, t)/\rho_a]$.

$Y_i(r, z, t)$ = total adsorbent phase concentration as a function of radial and axial position and time; $q_i(r, z, t) + [\epsilon_p C_{p,i}(r, z, t)/\rho_a]$.

$\bar{Y}_i(\bar{r}, \bar{z}, T)$ = reduced total adsorbent phase concentration as a function of dimensionless radial and axial position and dimensionless time (dimensionless); $Y_i(r, z, t)/Y_{e,i}$.

z = axial coordinate (m).

$\bar{z}$ = reduced axial coordinate (dimensionless); z/L.

ϵ = fraction of volumetric space in reactor unoccupied by adsorbent, or void fraction (dimensionless).

ϵ_p = fraction of volumetric space in adsorbent phase unoccupied by adsorbent on the pore volume fraction (dimensionless).

ρ_a = adsorbent density which includes pore volume (kg/m^3).

ρ_b = adsorbent bulk density (kg/m^3).

ρ_L = density of water (kg/m^3).

τ = fluid residence time in packed bed, or packed bed contact time (min).

τ_p = tortuosity of adsorbent (dimensionless).

μ = viscosity of water (kg/m · s).

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